Stereoselective Synthesis of Optically Active 3-Hydroxy-7,8-dihydro-β-ionol-glucosides

Yumiko YAMANO, Yuka SHIMIZU, and Masayoshi ITO*

Kobe Pharmaceutical University; Motoyamakita-machi, Higashinada-ku, Kobe 658–8558, Japan.
Received February 24, 2003; accepted April 16, 2003

A stereocontrolled synthesis of optically active β-D-glucopyronosides 6a, b and 11a, b was accomplished *via* the 7,8-saturated alcohols 4a, b, efficiently prepared by an asymmetric transfer hydrogenation of the α,β-acetylenic ketone 1 and subsequent catalytic hydrogenation. Simultaneous separation of these four glucosides by HPLC was also performed. This work is useful not only in order to confirm the stereochemistries of the trace amount of glucosides in plants but also to clarify their biosynthesis.

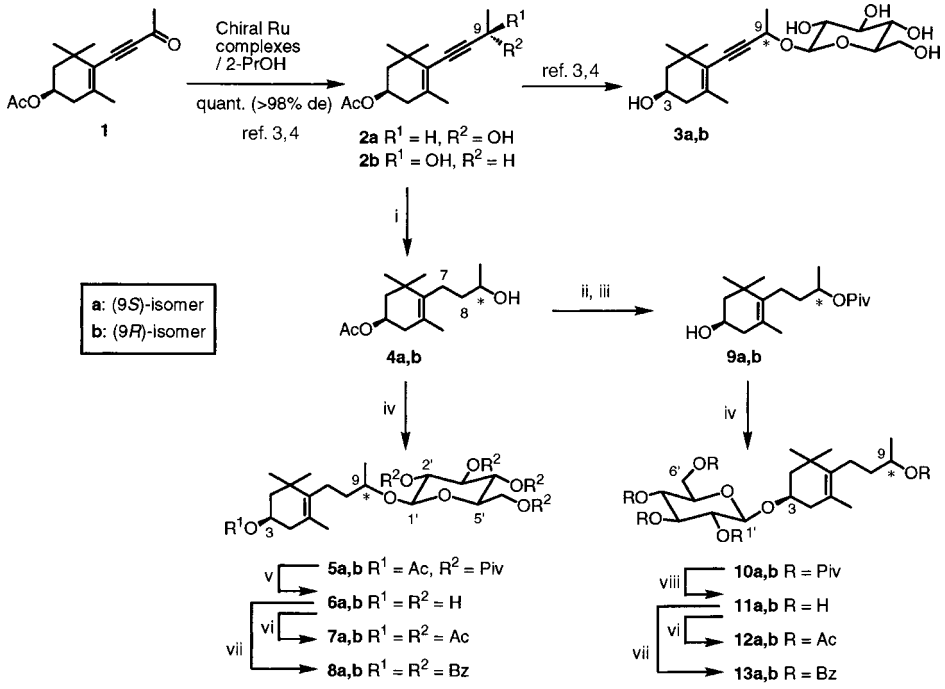
Key words 3-hydroxy-7,8-dihydro-β-ionol; β-D-glucopyronoside; stereocontrolled synthesis; HPLC separation

C_{13}-Norisoprenoid-glucosides **3**, **6**, **11** (Chart 1) have been isolated from rose petals[1] and have been suggested[2] to be produced through biodegradation of carotenoids in plants. In these glucosides, the acetylenic diol-glucoside **3** was considered[2] to be an important progenitor of damascenone, the key flavor compound in an essential oil of rose flowers. Their C-3 hydroxy groups are considered to be of β-configuration, because most natural xantophylls have β-configuration for C-3 hydroxy groups. However, their stereochemistries at C-9 were not confirmed.

Recently, we reported[3,4] stereocontrolled synthesis of (3*R*,9*S*)- and (3*R*,9*R*)-9-*O*-β-D-glucopyranosides **3a** and **3b** utilizing an asymmetric transfer hydrogenation[5] of the α,β-acetylenic ketone **1** catalyzed by chiral ruthenium complexes as the key step, leading to the confirmation of the stereochemistries of natural glucosides. We now wish to describe the stereoselective synthesis of (3*R*,9*S*)- and (3*R*,9*R*)-9-*O*-β-D-glucopyranosides **6a**, **b** and (3*R*,9*S*)- and (3*R*,9*R*)-3-*O*-β-D-glucopyranosides **11a**, **b** *via* hydrogenation of the chiral intermediates **2a**, **b**, in order to clarify the stereochemistries of the trace amount of glucosides in plants.

Results and Discussion

A catalytic hydrogenation of α-acetylenic alcohols **2a** and **2b** over palladium carbon in ethanol under a hydrogen atmosphere at room temperature (rt) provided the 7,8-saturated alcohols **4a** (78%) and **4b** (58%), respectively. β-Glucosidation[3,4] of **4a**, **b** was achieved (**5a**: 66%, **5b**: 87%) by use of tetra-*O*-pivaloyl (Piv)-α-D-glucopyranosyl bromide[6] possessing a sterically bulky acyloxy group at C-2 position as a glucosyl donor and silver triflate as an activator in the presence of *N*,*N*-tetramethylurea. The acyl groups of **5a**, **b** were re-



Reagents and conditions: i, Pd/C, H_2, EtOH; ii, PivCl, pyridine; iii, NaOMe, MeOH; iv, tetra-*O*-pivaloyl-α-D-glucopyranosyl bromide, AgOTf, $Me_2NC(O)NMe_2$; v, LiOH, MeOH, rt; vi, Ac_2O, pyridine; vii, BzCl, pyridine; viii, LiOH, MeOH, reflux.

Chart 1

* To whom correspondence should be addressed. e-mail: m-ito@kobepharma-u.ac.jp

Table 1. Characteristic ^{1}H- and ^{13}C-NMR Spectral Data (δ: ppm, in $CDCl_3$) for Pentaacetates **7a**, **b** and **12a**, **b**

	9-*O*-Glucosides			3-*O*-Glucosides		
	7a (3*R*,9*S*)	**7b** (3*R*,9*R*)	Glucocside from rose petals[1)]	**12a** (3*R*,9*S*)	**12b** (3*R*,9*R*)	Glucocside from rose petals[1)]
9-C$\underline{H}_3$	1.26	1.13	1.14	1.23	1.23	1.23
9-H	3.68	3.75	3.75	4.88	4.88	4.87
8-H_2	1.43	1.54	1.52	1.54	1.56	1.54
	1.59			1.64		
7-H_2	1.92	1.88	1.93	1.98	1.89	1.95
	2.06	2.19	2.07		2.06	2.05
1′-H	4.57	4.55	4.55	4.63	4.63	4.63
9-$\underline{C}H_3$	21.60	19.53 or 19.54	19.6	19.69 or 19.76	19.79	19.8
C7	24.11	23.73	23.7	23.91	23.96	23.9
C8	37.26	37.36	37.2	36.28	36.34	36.2
C9	79.21	76.20	76.4	71.34	71.32	71.3
C1′	101.24	99.17	99.2	99.43	99.43	99.6

Table 2. Characteristic ^{1}H- and ^{13}C-NMR Spectral Data (δ: ppm, in CD_3OD) for Pentaols **6a**, **b** and **11a**, **b**

	9-*O*-Glucosides			3-*O*-Glucosides		
	6a (3*R*,9*S*)	**6b** (3*R*,9*R*)	Glucocside from *Linaria japonica*[7)]	**11a** (3*R*,9*S*)	**11b** (3*R*,9*R*)	Glucocside from *Linaria japonica*[7)]
9-C$\underline{H}_3$	1.26	1.20	1.19	1.17	1.16	1.16
9-H	3.83	3.88	*ca.* 3.85	3.70	3.70	3.69
8-H_2	1.52	1.54	1.54	1.45	1.49	*ca.* 1.48
	ca. 1.66	*ca.* 1.64	*ca.* 1.67	1.53		
7-H_2	2.06	1.95	1.95	2.02	1.92	1.93
	2.15	2.24	2.24	2.12	2.21	2.20
1′-H	4.34	4.34	4.34	4.42	4.42	4.42
9-$\underline{C}H_3$	21.77	19.75	19.8	23.24	23.28	23.3
C7	25.02	25.34	25.3	25.54	25.56	25.6
C8	38.81	38.99	39.0	40.67	40.74	40.8
C9	77.87 or 77.88	76.12	76.2	69.17	69.20	69.2
C1′	103.88	102.24	102.2	102.33	102.35	102.4

moved under basic conditions to give the free alcohols **6a** (70%) and **6b** (98%). Since natural glucosides in rose petals were isolated[1)] as pentaacetates, pentaols **6a**, **b** were then acetylated to provide pentaacetates **7a** (97%) and **7b** (92%), respectively.

3-*O*-β-D-Glucopyranosides **10a** (48%) and **10b** (96%) were also prepared by the similar glucosidation of alcohols **9a**, **b**, which were derived (**9a**: 84%, **9b**: 99%) by pivaloylation of **4a**, **b** and subsequent deacetylation. Treatment of the pentapivaloate **10a** under the basic conditions used to cleave acyl groups of **5a**, **b** provided only the tetraol (95%), because of stability of C-9-pivaloate. This mono C-9-pivaloate was treated with lithium hydroxide in refluxing methanol to give the pentaol **11a** in 74% (70% from **10a**). Thus, the pentapivaloate **10b** was treated with lithium hydroxide in refluxing methanol to yield directly the pentaol **11b** in 70%. Finally, pentaols **11a**, **b** were acetylated to afford pentaacetates **12a** (93%) and **12b** (93%).

^{1}H- and ^{13}C-NMR spectra of 9-*O*-glucosides **7a**, **b** indicated characteristic differences around C-9 as shown in Table 1, while those of 3-*O*-glucosides **12a**, **b** were similar to each other but showed slight differences in protons at C-7 and C-8. Spectral data of pentaacetylated 9-*O*- and 3-*O*-glucosides isolated[1)] from rose petals were identical with those of synthetic (3*R*,9*R*)-glucosides **7b** and **12b**. The stereochemistry at C-9 of acetylenic diol-glucoside isolated from rose petals was already confirmed[3,4)] to be *R*. Therefore, it is presumed that there are some enzymes catalyzing stereoselective reduction of ketones to (*R*)-alcohols in rose flowers.

On the other hand, these glucosides were previously isolated[7)] from *Linaria japonica* as free alcohols. Their absolute configurations were proposed to be *R* at both C-3 and C-9 by the application of an empirical rule[8,9)] of β-D-glucosylation-induced shift trends. By comparison with ^{13}C-NMR data between glucosides and their aglycone alcohols, the absolute stereochemistries at the carbon possessing the glycosylated hydroxy group can be confirmed. However, determination of the absolute configuration at the carbon having the free hydroxy group (C-9 configuration of 3-*O*-glucoside as well as C-3 configuration of 9-*O*-glucoside) is difficult by the application of this empirical rule. In this time, stereochemistries of both the 3-*O*-glucoside and the 9-*O*-glucoside isolated from *Linaria japonica* could be confirmed to be of (3*R*,9*R*)-configuration by comparison of spectral data for our synthetic glucosides **6a**, **b** and **11a**, **b** as shown in Table 2.

In order to facilitate the confirmation of stereochemistries of natural glucosides, separation of synthetic four isomers **6a**, **b** and **11a**, **b** by HPLC was investigated. Since these glu-

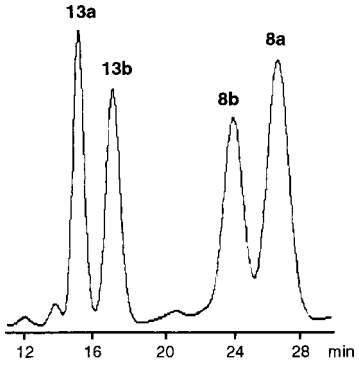


Fig. 1. HPLC Elution Profile of a Mixture of Glucosides **8a**, **8b**, **13a** and **13b**

Column: CHIRALPAK AD-H 0.46×25 cm; eluent: ethanol–hexane (15 : 85); flow rate: 0.7 ml/min; UV detection: 230 nm.

cosides did not show a remarkable UV absorption, they were detected as pentabenzoates **8a**, **b** and **13a**, **b** (Chart 1), respectively. Simultaneous separation using a chiral column (CHIRALPAK AD-H; DAICEL) was performed as shown in Fig. 1. Works to determine streochemistries of trace amount of glucosides in plants are now in progress.

Experimental

General ^{1}H- and ^{13}C-NMR spectra were obtained with a Varian Gemini-300 or a Varian VXR-500 superconducting FT-NMR spectrometer and the chemical shifts were referenced to tetramethylsilane. IR spectra were measured on a Perkin Elmer FT-IR spectrometer, model Paragon 1000. Mass spectra were taken on a Hitachi M-4100 spectrometer. Optical rotations were determined on a JASCO DIP-181 polarimeter. Column chromatography (CC) was performed on silica gel (Merck Art. 7734). Short-CC was conducted on silica gel (Merck Art. 7739) under reduced pressure. Evaporation of the extract or the filtrate was carried out under reduced pressure. Ether refers to diethyl ether, and hexane to *n*-hexane. NMR assignments are given using the retinoid numbering system.

(1*R*)-4-[(3*S*/*R*)-3-Hydroxybutyl]-3,5,5-trimethylcyclohex-3-enyl Acetate (4a/b) Catalytic hydrogenation of the (9*S*)-α-acetylenic alcohol **2a**[3,4] (1.23 g, 4.92 mmol) over 10% palladium carbon (250 mg) in EtOH (25 ml) under a hydrogen atmosphere at rt for 3 h and purification of the crude product by short-CC (ether–hexane, 1 : 2) gave the (9*S*)-7,8-saturated alcohol **4a** (970 mg, 78%). The compound **4b** was prepared (58%) in the same manner as described above.

4a: Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.07 (6H, s, *gem*-Me), 1.22 (3H, d, J=6.5 Hz, 9-Me), 1.41—1.59 (2H, m, 8-H_2), 1.53 (1H, t, J=12 Hz, 2ax-H), 1.62 (3H, s, 5-Me), 1.71 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 1.96—2.17 (3H, m, 4ax-H, 7-H_2), 2.04 (3H, s, OAc), 2.30 (1H, br dd, J=16.5, 5 Hz, 4eq-H), 3.80 (1H, sext-like, J=6 Hz, 9-H), 5.00 (1H, m, 3-H). IR ($CHCl_3$) cm^{-1}: 3610, 3459 (OH), 1724 (OCO). EI-MS *m*/*z*: 254.1885 [Calcd for $C_{15}H_{26}O_3$ (M^+) 254.1881]. $[\alpha]_D^{26}$ −44.6° (c=0.96, MeOH).

4b: Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.06, 1.07 (each 3H, s, *gem*-Me), 1.22 (3H, d, J=6.5 Hz, 9-Me), 1.47—1.55 (2H, m, 8-H_2), 1.53 (1H, t, J=12 Hz, 2ax-H), 1.62 (3H, s, 5-Me), 1.72 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), *ca.* 1.92 (1H, m, 7-H), 2.03 (1H, br dd, J=16, 10 Hz, 4ax-H), 2.04 (3H, s, OAc), *ca.* 2.19 (1H, m, 7-H), 2.30 (1H, br dd, J=16, 6 Hz, 4eq-H), 3.80 (1H, m, 9-H), 5.00 (1H, m, 3-H). IR ($CHCl_3$) cm^{-1}: 3611, 3468 (OH), 1724 (OCO). EI-MS *m*/*z*: 254.1895 [Calcd for $C_{15}H_{26}O_3$ (M^+) 254.1881]. $[\alpha]_D^{25}$ −53.0° (c=0.98, MeOH).

(1*R*)-4-[(3*S*/*R*)-3-(2,2-Dimethyl-1-oxopropyloxy)]-3,5,5-trimethylcyclohex-3-enol (9a/b) The (9*S*)-alcohol **4a** (740 mg, 2.9 mmol) was dissolved in pyridine (1 ml), then pivaloyl chloride (0.72 ml, 6.1 mmol) was added to it. After being stirred under an argon atmosphere at rt for 15 h, the reaction mixture was poured into ice-water and extracted with ether. The extracts were washed successively with aq. 5% HCl, saturated aq. $NaHCO_3$, and brine. Evaporation of the dried extracts gave the pivaloate, which without purification was dissolved in MeOH (35 ml) and NaOMe (1 M in MeOH; 3.5 ml, 3.5 mmol) was added to it. The reaction mixture was stirred under an argon atmosphere at rt for 2 h. To this mixture was added Dowex 50W-X8 (H^+) (3.5 g) and stirring continued at rt for a further 10 min. After Dowex was filtered off, the filtrate was evaporated to give a residue, which was purified by short-CC (acetone–hexane, 15 : 85) to give the 3-hydroxy compound **9a** (727 mg, 84% from **4a**). The compound **9b** was prepared (99%) in the same manner as described above.

9a: Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.01, 1.06 (each 3H, s, *gem*-Me), 1.21 (3H, d, J=6.5 Hz, 9-Me), 1.21 (9H, s, *tert*-Bu), 1.42 (1H, t, J=12 Hz, 2ax-H), 1.53—1.68 (2H, m, 8-H_2), 1.62 (3H, s, 5-Me), 1.71 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 1.96 (1H, br dd, J=16, 10 Hz, 4ax-H), 2.00 (2H, t, J=8.5 Hz, 7-H_2), 2.23 (1H, ddd, J=16, 5, 2 Hz, 4eq-H), 3.92 (1H, m, 3-H), 4.87 (1H, sext-like, J=6 Hz, 9-H). IR ($CHCl_3$) cm^{-1}: 3606, 3480 (OH), 1715 (OCO). EI-MS *m*/*z*: 296.2359 [Calcd for $C_{18}H_{32}O_3$ (M^+) 296.2350]. $[\alpha]_D^{25}$ −60.0° (c=0.95, MeOH).

9b: Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.02, 1.04 (each 3H, s, *gem*-Me), 1.21 (3H, d, J=6.5 Hz, 9-Me), 1.21 (9H, s, *tert*-Bu), 1.42 (1H, t, J=12 Hz, 2ax-H), 1.55—1.62 (2H, m, 8-H_2), 1.62 (3H, s, 5-Me), 1.71 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 1.89 (1H, m, 7-H), 1.97 (1H, br dd, J=16, 10 Hz, 4ax-H), 2.11 (1H, m, 7-H), 2.23 (1H, ddd, J=16, 5.5, 2 Hz, 4eq-H), 3.93 (1H, m, 3-H), 4.86 (1H, sext-like, J=6 Hz, 9-H). IR ($CHCl_3$) cm^{-1}: 3606, 3467 (OH), 1715 (OCO). EI-MS *m*/*z*: 296.2350 [Calcd for $C_{18}H_{32}O_3$ (M^+) 296.2350]. $[\alpha]_D^{29}$ −32.8° (c=0.98, MeOH).

β-Glucosidation of Alcohols 4a, b and 9a, b Under a nitrogen stream, AgOTf (2.41 g, 9.37 mmol) was added to a stirred suspension of tetra-*O*-pivaloyl-α-D-glucosyl bromide[6] (4.21 g, 7.52 mmol), (3*R*,9*S*)-9-hydroxy compound **4a** (955 mg, 3.76 mmol), *N*,*N*-tetramethylurea (1.8 ml, 15 mmol) and powdered molecular sieves 4A (10 g) in dry CH_2Cl_2 (40 ml) at 0 °C. After being stirred at 0 °C for 30 min and rt for 2 h, the reaction was quenched with saturated aq. $NaHCO_3$. The reaction mixture was diluted with AcOEt and filtered through Celite. The organic layer of the filtrate was washed with brine, dried and evaporated to give a residue, which was purified by CC (CH_2Cl_2–hexane–ether, 5 : 4 : 0.7) to afford the β-glucoside **5a** (1.87 g, 66%). The glucosides **5b** (87%), **10a** (48%) and **10b** (96%) were prepared in the same manner as described above.

5a: Colorless foams; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.03, 1.04 (each 3H, s, *gem*-Me), 1.11, 1.14, 1.16, 1.22 (each 9H, s, *tert*-Bu×4), 1.26 (3H, d, J=6 Hz, 9-Me), 1.42 (1H, m, 8-H), 1.51 (1H, t, J=12 Hz, 2ax-H), 1.57 (3H, s, 5-Me), 1.61 (1H, m, 8-H), 1.71 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 1.96—2.06 (3H, m, 4ax-H, 7-H_2), 2.04 (3H, s, OAc), 2.29 (1H, br dd, J=16, 6 Hz, 4eq-H), 3.67 (1H, sext, J=6 Hz, 9-H), 3.73 (1H, ddd, J=9.5, 6.5, 2 Hz, 5′-H), 4.00 (1H, dd, J=12, 6.5 Hz, 6′-H), 4.23 (1H, dd, J=12, 2 Hz, 6′-H), 4.59 (1H, d, J=8 Hz, 1′-H), 4.98 (1H, m, 3-H), 5.03 (1H, dd, J=9.5, 8 Hz, 2′-H), 5.05 (1H, t, J=9.5 Hz, 4′-H), 5.33 (1H, t, J=9.5 Hz, 3′-H). IR ($CHCl_3$) cm^{-1}: 1739 (OCO). SIMS *m*/*z*: 775.4603 [Calcd for $C_{41}H_{68}O_{12}Na$ (M^++Na) 775.4604]. $[\alpha]_D^{26}$ −32.0° (c=1.00, $CHCl_3$).

5b: Colorless foams; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.04 (6H, s, *gem*-Me), 1.11 (3H, d, J=6 Hz, 9-Me), 1.11 (9H), 1.15 (18H), 1.21 (9H) (each s, *tert*-Bu×4), 1.50 (1H, t, J=12 Hz, 2ax-H), *ca.* 1.52 (2H, m, 8-H_2), 1.58 (3H, s, 5-Me), 1.70 (1H, ddd, J=12, 3.5, 1.5 Hz, 2eq-H), 1.87 (1H, br td, J=12, 5.5 Hz, 7-H), 2.03 (3H, s, OAc), 2.00 (1H, br dd, J=16.5, 9.5 Hz, 4ax-H), 2.22 (1H, br td, J=12, 6.5 Hz, 7-H), 2.28 (1H, br dd, J=16.5, 5.5 Hz, 4eq-H), 3.70 (1H, ddd, J=9.5, 5.5, 2 Hz, 5′-H), 3.78 (1H, sext, J=6 Hz, 9-H), 4.01 (1H, dd, J=12.5, 5.5 Hz, 6′-H), 4.24 (1H, dd, J=12.5, 2 Hz, 6′-H), 4.59 (1H, d, J=8 Hz, 1′-H), 4.99 (1H, m, 3-H), 5.01 (1H, dd, J=9.5, 8 Hz, 2′-H), 5.12 (1H, t, J=9.5 Hz, 4′-H), 5.32 (1H, t, J=9.5 Hz, 3′-H). IR ($CHCl_3$) cm^{-1}: 1739 (OCO). SIMS *m*/*z*: 775.4603 [Calcd for $C_{41}H_{68}O_{12}Na$ (M^++Na) 775.4604]. $[\alpha]_D^{27}$ −41.8° (c=1.00, MeOH).

10a: Colorless foams; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.99, 1.03 (each 3H, s, *gem*-Me), 1.11 (9H), 1.16 (18H), 1.20 (9H), 1.21 (9H) (each s, *tert*-Bu×5), 1.20 (3H, d, J=6.5 Hz, 9-Me), 1.46 (1H, t, J=12 Hz, 2ax-H), 1.50—1.68 (2H, m, 8-H_2), 1.59 (3H, s, 5-Me), 1.78 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 1.94 (1H, br dd, J=16, 5 Hz, 4eq-H), 1.98 (2H, br t, J=8.5 Hz, 7-H_2), 2.17 (1H, br dd, J=16, 5 Hz, 4eq-H), 3.74 (1H, ddd, J=9.5, 6.5, 2 Hz, 5′-H), 3.93 (1H, m, 3-H), 4.00 (1H, dd, J=12.5, 6.5 Hz, 6′-H), 4.25 (1H, dd, J=12.5, 2 Hz, 6′-H), 4.67 (1H, d, J=8 Hz, 1′-H), 4.86 (1H, sext-like, J=6.5 Hz, 9-H), 5.00 (1H, dd, J=9.5, 8 Hz, 2′-H), 5.07 (1H, t, J=9.5 Hz, 4′-H), 5.33 (1H, t, J=9.5 Hz, 3′-H). IR ($CHCl_3$) cm^{-1}: 1739 (OCO). SIMS *m*/*z*: 817.5051 [Calcd for $C_{44}H_{74}O_{12}Na$ (M^++Na) 817.5074]. $[\alpha]_D^{25}$ −45.5° (c=1.05, $CHCl_3$).

10b: Colorless foams; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.99, 1.02 (each 3H, s, *gem*-Me), 1.111, 1.157, 1.160, 1.202, 1.213 (each 9H, s, *tert*-Bu×5), 1.20 (3H, d, J=6.5 Hz, 9-Me), 1.46 (1H, t, J=12 Hz, 2ax-H), 1.51—1.63 (2H, m, 8-H_2), 1.59 (3H, s, 5-Me), 1.78 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 1.88 (1H, br dt, J=13, 8 Hz, 7-H), 1.94 (1H, br dd, J=16.5, 10 Hz, 4ax-H), 2.07 (1H, m, 7-H), 2.17 (1H, br dd, J=16.5, 5 Hz, 4eq-H), 3.74 (1H, ddd, J=9.5, 6.5, 2 Hz, 5′-H), 3.92 (1H, m, 3-H), 4.00 (1H, dd, J=12.5, 6.5 Hz,

6′-H), 4.25 (1H, dd, J=12.5, 2 Hz, 6′-H), 4.67 (1H, d, J=8 Hz, 1′-H), 4.85 (1H, sext, J=6.5 Hz, 9-H), 5.00 (1H, dd, J=9.5, 8 Hz, 2′-H), 5.07 (1H, t, J=9.5 Hz, 4′-H), 5.33 (1H, t, J=9.5 Hz, 3′-H). IR ($CHCl_3$) cm^{-1}: 1740 (OCO). SIMS m/z: 817.5087 [Calcd for $C_{44}H_{74}O_{12}Na$ (M^++Na) 817.5073]. $[\alpha]_D^{25}$ −11.8° (c=1.01, $CHCl_3$).

(1*S*/*R*)-3-[(4*R*)-4-Hydroxy-2,6,6-trimethylcyclohex-1-enyl]-1-methylpropyl-β-D-glucopyranoside (6a/b) To a solution of the tetrapivaloate **5a** (2.36 g, 3.14 mmol) in MeOH (50 ml) was added $LiOH \cdot H_2O$ (300 mg, 7.14 mmol) and the mixture was stirred under an argon atmosphere at rt for 20 h. To this mixture was added Dowex 50W-X8 (H^+) (8 g) and stirring continued at rt for a further 10 min. After Dowex was filtered off, the filtrate was evaporated to give a residue, which was purified by short-CC (MeOH–CH_2Cl_2, 15 : 85) to afford the pentaol **6a** (820 mg, 70%). The compound **6b** was prepared (98%) in the same manner as described above. ^{1}H- and ^{13}C-NMR data of the synthetic (3*R*,9*R*)-9-*O*-glucoside **6b** were in agreement with those of the 9-*O*-glucoside isolated[7] from *Linaria japonica*.

6a: Colorless foams; ^{1}H-NMR (500 MHz, CD_3OD) δ: 1.04, 1.07 (each 3H, s, *gem*-Me), 1.26 (3H, d, J=6 Hz, 9-Me), 1.38 (1H, t, J=12 Hz, 2ax-H), 1.52 (1H, m, 8-H), 1.64 (3H, s, 5-Me), *ca.* 1.66 (1H, m, 8-H), 1.67 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 1.92 (1H, br dd, J=16, 10 Hz, 4ax-H), 2.06, 2.15 (each 1H, br td, J=13, 5 Hz, 7-H_2), 2.18 (1H, br dd, J=16, 5.5 Hz, 4eq-H), 3.16 (1H, dd, J=9, 8 Hz, 2′-H), 3.24 (1H, ddd, J=9, 5.5, 2 Hz, 5′-H), 3.28 (1H, t, J=9 Hz, 4′-H), 3.34 (1H, t, J=9 Hz, 3′-H), 3.66 (1H, dd, J=12, 5.5 Hz, 6′-H), 3.83 (1H, sext, J=6 Hz, 9-H), *ca.* 3.84 (1H, m, 3-H), 3.85 (1H, dd, J=12, 2 Hz, 6′-H), 4.34 (1H, d, J=8 Hz, 1′-H). ^{13}C-NMR (125 MHz, CD_3OD) δ: 20.08 (5-CH_3), 21.77 (9-CH_3), 25.02 (C7), 28.90, 30.30 (*gem*-CH_3), 37.96 (C1), 38.81 (C8), 42.96 (C4), 49.53 (C2), 62.83 (C6′), 65.68 (C3), 71.72 (C4′), 75.33 (C2′), 77.87, 77.88 (C5′, C9), 78.29 (C3′), 103.88 (C1′), 125.43 (C5), 138.36 (C6). SIMS m/z: 373.2222 [Calcd for $C_{19}H_{33}O_7$ (M^-−H) 373.2223]. $[\alpha]_D^{23}$ −74.2° (c=0.97, MeOH).

6b: Colorless foams; ^{1}H-NMR (500 MHz, CD_3OD) δ: 1.03, 1.05 (each 3H, s, *gem*-Me), 1.20 (3H, d, J=6 Hz, 9-Me), 1.37 (1H, t, J=12 Hz, 2ax-H), 1.54 (1H, tt, J=13, 5.5 Hz, 8-H), 1.63 (3H, s, 5-Me), *ca.* 1.64 (1H, m, 8-H), 1.67 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 1.92 (1H, br dd, J=16, 10 Hz, 4ax-H), 1.95 (1H, br td, J=13, 5 Hz, 7-H), 2.17 (1H, br dd, J=16, 5 Hz, 4eq-H), 2.24 (1H, br td, J=13, 4.5 Hz, 7-H), 3.15 (1H, dd, J=9, 8 Hz, 2′-H), 3.25 (1H, ddd, J=9, 5.5, 2 Hz, 5′-H), 3.29 (1H, t, J=9 Hz, 4′-H), 3.36 (1H, t, J=9 Hz, 3′-H), 3.67 (1H, dd, J=12, 5.5 Hz, 6′-H), *ca.* 3.84 (1H, m, 3-H), 3.85 (1H, dd, J=12, 2 Hz, 6′-H), 3.88 (1H, sext, J=6 Hz, 9-H), 4.34 (1H, d, J=8 Hz, 1′-H). ^{13}C-NMR (125 MHz, CD_3OD) δ: 19.75 (9-CH_3), 20.08 (5-CH_3), 25.34 (C7), 28.91, 30.40 (*gem*-CH_3), 38.84 (C1), 38.99 (C8), 42.99 (C4), 49.55 (C2), 62.96 (C6′), 65.73 (C3), 71.86 (C4′), 75.24 (C2′), 76.12 (C9), 77.89 (C5′), 78.25 (C3′), 102.24 (C1′), 125.39 (C5), 138.49 (C6). SIMS m/z: 373.2223 [Calcd for $C_{19}H_{33}O_7$ (M^-−H) 373.2223]. $[\alpha]_D^{27}$ −64.5° (c=0.99, MeOH).

(1*R*)-4-[(3*S*)-3-Hydroxybutyl]-3,5,5-trimethylcyclohex-3-enyl-β-D-glucopyranoside (11a) In the same manner as described for the preparation of the pentaols **6a**, **b**, the pentapivaloate **10a** (876 mg) was treated with $LiOH \cdot H_2O$ (112 mg, 2.67 mmol) to afford the mono 9-*O*-pivaloate (479 mg, 95%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.01, 1.02 (each 3H, s, *gem*-Me), 1.20 (3H, d, J=6.5 Hz, 9-Me), 1.20 (9H, s, *tert*-Bu), 1.50 (1H, t, J=12.5 Hz, 2ax-H), 1.56 (2H, m, 8-H_2), 1.60 (3H, s, 5-Me), 1.80 (1H, br d, J=12.5 Hz, 2eq-H), 1.99 (2H, br t, J=8.5 Hz, 7-H_2), 2.03 (1H, br dd, J=16.5, 10.5 Hz, 4ax-H), 2.29 (1H, br dd, J=16.5, 5 Hz, 4eq-H), 3.31 (1H, br d, J=9 Hz, 5′-H), 3.40 (1H, br t, J=9 Hz, 2′-H), 3.56 (1H, br t, J=9.5 Hz, 4′-H), 3.66 (1H, br t, J=9.5 Hz, 3′-H), 3.85 (2H, m, 6′-H_2), 3.97 (1H, m, 3-H), 4.46 (1H, d, J=7.5 Hz, 1′-H), 4.86 (1H, sext, J=6.5 Hz, 9-H). SIMS m/z: 457.2808 [Calcd for $C_{24}H_{41}O_8$ (M^-−H) 457.2799]. A solution of this mono 9-*O*-pivaloate (479 mg) in MeOH (15 ml) containing $LiOH \cdot H_2O$ (120 mg, 2.86 mmol) was refluxed under an argon atmosphere for 20 h. Work-up gave a residue, which was purified by short-CC (MeOH–CH_2Cl_2, 15 : 85) to give the pentaol **11a** (290 mg, 74%; 70% from **10a**).

11a: Colorless foams; ^{1}H-NMR (500 MHz, CD_3OD) δ: 1.05, 1.07 (each 3H, s, *gem*-Me), 1.17 (3H, d, J=6 Hz, 9-Me), 1.45 (1H, m, 8-H), 1.49 (1H, t, J=12 Hz, 2ax-H), 1.53 (1H, m, 8-H), 1.64 (3H, s, 5-Me), 1.83 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 2.01 (1H, br dd, J=16.5, 9 Hz, 4ax-H), *ca.* 2.02 (1H, m, 7-H), 2.12 (1H, br td, J=12.5, 5 Hz, 7-H), 2.34 (1H, br dd, J=16.5, 5 Hz, 4eq-H), 3.15 (1H, dd, J=9, 8 Hz, 2′-H), 3.29 (2H, m, 4′-H, 5′-H), 3.35 (1H, t, J=9 Hz, 3′-H), 3.67 (1H, dd, J=12, 5 Hz, 6′-H), 3.70 (1H, sext, J=6 Hz, 9-H), 3.86 (1H, dd, J=12, 2 Hz, 6′-H), 4.05 (1H, m, 3-H), 4.42 (1H, d, J=8 Hz, 1′-H). ^{13}C-NMR (125 MHz, CD_3OD) δ: 20.02 (5-CH_3), 23.24 (9-CH_3), 25.54 (C7), 28.81, 30.27 (*gem*-CH_3), 38.78 (C1), 39.78 (C4), 40.67 (C8), 47.50 (C2), 62.75 (C6′), 69.17 (C9), 71.67 (C4′), 73.27 (C3), 75.18 (C2′), 77.87 (C5′), 78.13 (C3′), 102.33 (C1′), 125.09 (C5), 138.54 (C6). SIMS m/z: 373.2244 [Calcd for $C_{19}H_{33}O_7$ (M^-−H) 373.2223]. $[\alpha]_D^{25}$ −53.2° (c=1.00, MeOH).

(1*R*)-4-[(3*R*)-3-Hydroxybutyl]-3,5,5-trimethylcyclohex-3-enyl-β-D-glucopyranoside (11b) A solution of the pentapivaloate **10b** (1.17 g, 1.47 mmol) in MeOH (25 ml) containing $LiOH \cdot H_2O$ (450 mg, 10.7 mmol) was refluxed under an argon atmosphere for 20 h. To this mixture was added Dowex 50W-X8 (H^+) (6.5 g) and stirring continued at rt for a further 10 min. After Dowex was filtered off, the filtrate was evaporated to give a residue, which was purified by short-CC (MeOH–CH_2Cl_2, 15 : 85) to afford the pentaol **11b** (403 mg, 73%). ^{1}H- and ^{13}C-NMR data of the synthetic (3*R*,9*R*)-3-*O*-glucoside **11b** were in agreement with those of the 3-*O*-glucoside isolated[7] from *Linaria japonica*.

11b: Colorless foams; ^{1}H-NMR (300 MHz, CD_3OD) δ: 1.05, 1.06 (each 3H, s, *gem*-Me), 1.16 (3H, d, J=6 Hz, 9-Me), 1.49 (2H, m, 8-H_2), 1.49 (1H, t, J=12 Hz, 2ax-H), 1.65 (3H, s, 5-Me), 1.83 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 1.92 (1H, m, 7-H), 2.01 (1H, br dd, J=16, 9.5 Hz, 4ax-H), 2.21 (1H, m, 7-H), 2.34 (1H, br dd, J=16, 5 Hz, 4eq-H), 3.15 (1H, dd, J=9, 8 Hz, 2′-H), 3.29 (2H, m, 4′-H, 5′-H), 3.36 (1H, t, J=9 Hz, 3′-H), 3.67 (1H, dd, J=12, 5 Hz, 6′-H), 3.70 (1H, sext, J=6 Hz, 9-H), 3.86 (1H, dd, J=12, 2 Hz, 6′-H), 4.06 (1H, m, 3-H), 4.42 (1H, d, J=8 Hz, 1′-H). ^{13}C-NMR (75 MHz, CD_3OD) δ: 20.05 (5-CH_3), 23.28 (9-CH_3), 25.56 (C7), 28.84, 30.31 (*gem*-CH_3), 38.80 (C1), 39.80 (C4), 40.74 (C8), 47.51 (C2), 62.76 (C6′), 69.20 (C9), 71.69 (C4′), 73.28 (C3), 75.21 (C2′), 77.90 (C5′), 78.16 (C3′), 102.35 (C1′), 125.12 (C5), 138.54 (C6). SIMS m/z: 373.2236 [Calcd for $C_{19}H_{33}O_7$ (M^-−H) 373.2223]. $[\alpha]_D^{25}$ −67.7° (c=0.96, MeOH).

Acetylation of Pentaols 6a, b and 11a, b To a solution of the pentaol **6a** (220 mg, 0.59 mmol) in pyridine (3.8 ml) was added Ac_2O (0.96 ml) and the mixture was stirred under an argon atmosphere at rt for 20 h, poured into ice-water and extracted with AcOEt. The extracts were washed successively with aq. 5% HCl, saturated aq. $NaHCO_3$, and brine. Evaporation of the dried extracts gave a residue, which was purified by CC (ether–CH_2Cl_2, 15 : 85) to afford the pentaacetate **7a** (334 mg, 97%). The compounds **7b** (92%), **12a** (93%) and **12b** (93%) were prepared in the same manner as described above. ^{1}H- and ^{13}C-NMR data of the synthetic (3*R*,9*R*)-9-*O*-glucoside **7b** and (3*R*,9*R*)-3-*O*-glucoside **12b** were in agreement with those of glucosides isolated[1] from rose petals.

7a: Colorless foams; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.03, 1.04 (each 3H, s, *gem*-Me), 1.26 (3H, d, J=6 Hz, 9-Me), 1.43 (1H, tt, J=13.5, 4.5 Hz, 8-H), 1.51 (1H, t, J=12.5 Hz, 2ax-H), 1.58 (3H, s, 5-Me), 1.59 (1H, m, 8-H), 1.71 (1H, ddd, J=12.5, 3.5, 2 Hz, 2eq-H), 1.92 (1H, br td, J=13.5, 4.5 Hz, 7-H), 2.004, 2.018, 2.027, 2.032, 2.079 (each 3H, s, OAc×5), 2.02 (1H, 4ax-H), 2.06 (1H, 7-H), 2.29 (1H, br dd, J=16.5, 5.5 Hz, 4eq-H), 3.68 (1H, m, 9-H), 3.71 (1H, ddd, J=10, 5.5, 2.5 Hz, 5′-H), 4.14 (1H, dd, J=12, 2.5 Hz, 6′-H), 4.25 (1H, dd, J=12, 5.5 Hz, 6′-H), 4.57 (1H, d, J=8 Hz, 1′-H), 4.98 (1H, m, 3-H), 5.00 (1H, dd, J=9.5, 8 Hz, 2′-H), 5.06 (1H, t, J=9.5 Hz, 4′-H), 5.21 (1H, t, J=9.5 Hz, 3′-H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 19.61 (5-CH_3), 20.61 20.62, 20.74, 20.75, 21.46 ($\underline{C}H_3CO$×5), 21.60 (9-CH_3), 24.11 (C7), 28.27, 29.45 (*gem*-CH_3), 37.26 (C8), 37.44 (C1), 38.14 (C4), 44.18 (C2), 62.26 (C6′), 68.59, 68.67 (C3, C4′), 71.69, 71.75 (C2′, C5′), 73.07 (C3′), 79.21 (C9), 101.24 (C1′), 123.90 (C5), 136.86 (C6), 169.17, 169.44, 170.37, 170.68, 170.85 (CO×5). IR ($CHCl_3$) cm^{-1}: 1755 (OCO). SIMS m/z: 607.2739 [Calcd for $C_{29}H_{44}O_{12}Na$ (M^++Na) 607.2728]. $[\alpha]_D^{25}$ −28.5° (c=0.95, MeOH).

7b: Colorless foams; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.04, 1.05 (each 3H, s, *gem*-Me), 1.13 (3H, d, J=6.5 Hz, 9-Me), 1.51 (1H, t, J=12 Hz, 2ax-H), 1.54 (2H, ddd, J=9, 7.5, 6.5 Hz, 8-H_2), 1.59 (3H, s, 5-Me), 1.70 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 1.88 (1H, br dt, J=15, 7.5 Hz, 7-H), *ca.* 2.01 (1H, 4ax-H), 2.006, 2.026, 2.030, 2.034, 2.066 (each 3H, s, OAc×5), 2.19 (1H, br dt, J=15, 9 Hz, 7-H), 2.28 (1H, br dd, J=16.5, 5.5 Hz, 4eq-H), 3.68 (1H, ddd, J=9.5, 5, 3 Hz, 5′-H), 3.75 (1H, sext, J=6.5 Hz, 9-H), 4.14 (1H, dd, J=12, 3 Hz, 6′-H), 4.23 (1H, dd, J=12, 5 Hz, 6′-H), 4.55 (1H, d, J=7.5 Hz, 1′-H), 4.96 (1H, dd, J=9.5, 7.5 Hz, 2′-H), 4.99 (1H, m, 3-H), 5.09 (1H, t, J=9.5 Hz, 4′-H), 5.21 (1H, t, J=9.5 Hz, 3′-H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 19.53, 19.54 (9-CH_3, 5-CH_3), 20.62, 20.65, 20.66, 20.70, 21.47 ($\underline{C}H_3CO$×5), 23.73 (C7), 28.27, 29.47 (*gem*-CH_3), 37.36 (C8), 37.46 (C1), 38.19 (C4), 44.25 (C2), 62.20 (C6′), 68.72 (C3, C4′), 71.62, 71.64 (C2′, C5′), 73.00 (C3′), 76.20 (C9), 99.17 (C1′), 123.70 (C5), 137.13 (C6), 169.23, 169.44, 170.37, 170.63 170.82 (CO×5). IR ($CHCl_3$) cm^{-1}: 1755 (OCO). SIMS m/z: 607.2748 [Calcd for $C_{29}H_{44}O_{12}Na$ (M^++Na) 607.2728]. $[\alpha]_D^{26}$ −41.0° (c=0.93, MeOH).

12a: Colorless foams; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.01, 1.04 (each 3H, s, *gem*-Me), 1.23 (3H, d, J=6 Hz, 9-Me), 1.49 (1H, t, J=12 Hz, 2ax-H), 1.54 (1H, m, 8-H), 1.60 (3H, s, 5-Me), 1.64 (1H, m, 8-H), 1.79 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 1.94 (1H, br dd, J=16.5, 9 Hz, 4ax-H), 1.98 (2H,

m, 7-H_2), 2.01 (3H), 2.03 (3H), 2.04 (6H), 2.08 (3H) (each s, OAc×5), 2.18 (1H, br dd, J=16.5, 5.5 Hz, 4eq-H), 3.70 (1H, ddd, J=9.5, 5, 2.5 Hz, 5′-H), 3.91 (1H, m, 3-H), 4.13 (1H, dd, J=12, 2.5 Hz, 6′-H), 4.25 (1H, dd, J=12, 5 Hz, 6′-H), 4.63 (1H, d, J=8 Hz, 1′-H), 4.88 (1H, sext, J=6 Hz, 9-H), 4.96 (1H, dd, J=9.5, 8 Hz, 2′-H), 5.07 (1H, t, J=9.5 Hz, 4′-H), 5.21 (1H, t, J=9.5 Hz, 3′-H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 19.69, 19.76 (5-CH_3, 9-CH_3), 20.61 20.64, 20.69, 20.75, 21.34 ($\underline{C}H_3CO$×5), 23.91 (C7), 28.49, 29.53 (*gem*-CH_3), 36.28 (C8), 37.60 (C1), 38.72 (C4), 45.89 (C2), 62.32 (C6′), 68.70 (C4′), 71.34 (C9), 71.57 (C2′), 71.76 (C5′), 72.94 (C3′), 73.47 (C3), 99.43 (C1′), 123.65 (C5), 137.11 (C6), 169.26, 169.44, 170.37, 170.68, 170.82 (CO×5). IR ($CHCl_3$) cm^{-1}: 1755 (OCO). SIMS *m*/*z*: 607.2726 [Calcd for $C_{29}H_{44}O_{12}Na$ (M^++Na) 607.2728]. $[\alpha]_D^{26}$ −43.7° (*c*=0.94, MeOH).

12b: Colorless foams; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.01, 1.02 (each 3H, s, *gem*-Me), 1.23 (3H, d, J=6 Hz, 9-Me), 1.49 (1H, t, J=12 Hz, 2ax-H), 1.56 (2H, m, 8-H_2), 1.61 (3H, s, 5-Me), 1.79 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 1.89 (1H, br td, J=13, 5 Hz, 7-H), 1.94 (1H, br dd, J=16, 9.5 Hz, 4ax-H), 2.01 (3H), 2.03 (3H), 2.04 (6H), 2.08 (3H) (each s, OAc×5), 2.06 (1H, m, 7-H), 2.18 (1H, br dd, J=16, 5.5 Hz, 4eq-H), 3.70 (1H, ddd, J=9.5, 5, 2.5 Hz, 5′-H), 3.91 (1H, m, 3-H), 4.13 (1H, dd, J=12, 2.5 Hz, 6′-H), 4.25 (1H, dd, J=12, 5 Hz, 6′-H), 4.63 (1H, d, J=8 Hz, 1′-H), 4.88 (1H, sext, J=6 Hz, 9-H), 4.96 (1H, dd, J=9.5, 8 Hz, 2′-H), 5.07 (1H, t, J=9.5 Hz, 4′-H), 5.21 (1H, t, J=9.5 Hz, 3′-H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 19.63 (5-CH_3), 19.79 (9-CH_3), 20.61, 20.64, 20.69, 20.75, 21.34 ($\underline{C}H_3CO$×5), 23.96 (C7), 28.46, 29.51 (*gem*-CH_3), 36.34 (C8), 37.59 (C1), 38.72 (C4), 45.87 (C2), 62.32 (C6′), 68.70 (C4′), 71.32 (C9), 71.57 (C2′), 71.77 (C5′), 72.94 (C3′), 73.47 (C3), 99.43 (C1′), 123.65 (C5), 137.07 (C6), 169.25, 169.43, 170.35, 170.66, 170.80 (CO×5). IR ($CHCl_3$) cm^{-1}: 1755 (OCO). SIMS *m*/*z*: 607.2750 [Calcd for $C_{29}H_{44}O_{12}Na$ (M^++Na) 607.2728]. $[\alpha]_D^{25}$ −28.3° (*c*=0.88, MeOH).

Benzoylation of Pentaols 6a, b and 11a, b To a solution of the pentaol **6a** (18.4 mg, 0.049 mmol) in pyridine (1.0 ml) was added benzoyl chloride (0.20 ml) and the mixture was stirred under an argon atmosphere at rt for 20 h, poured into ice-water and extracted with AcOEt. The extracts were washed successively with aq. 5% HCl, saturated aq. $NaHCO_3$, and brine. Evaporation of the dried extracts gave a residue, which was purified by short-CC (AcOEt–hexane, 15 : 85) to yield the pentabenzoate **8a** (39.4 mg, 90%). The compounds **8b** (51%), **13a** (88%) and **13b** (77%) were prepared in the same manner as described above.

8a: Colorless foams; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.78, 0.83 (each 3H, s, *gem*-Me), 1.29 (3H, d, J=6 Hz, 9-Me), *ca.* 1.37 (1H, m, 8-H), 1.53 (1H, t, J=12 Hz, 2ax-H), 1.42 (3H, s, 5-Me), *ca.* 1.54 (1H, m, 8-H), 1.73 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 1.76 (1H, m, 7-H), 1.95 (1H, br td, J=13, 4.5 Hz, 7-H), 2.07 (1H, br dd, J=16.5, 10 Hz, 4ax-H), 2.30 (1H, br dd, J=16.5, 5.5 Hz, 4eq-H), 3.73 (1H, m, 9-H), 4.18 (1H, ddd, J=10, 6, 3.5 Hz, 5′-H), 4.51 (1H, dd, J=12, 6 Hz, 6′-H), 4.65 (1H, dd, J=12, 3.5 Hz, 6′-H), 4.92 (1H, d, J=8 Hz, 1′-H), 5.13 (1H, m, 3-H), 5.57 (1H, dd, J=10, 8 Hz, 2′-H), 5.64 (1H, t, J=10 Hz, 4′-H), 5.92 (1H, t, J=10 Hz, 3′-H), 7.25—7.58 (15H, m, ArH), 7.82—8.06 (10H, m, ArH). SIMS *m*/*z*: 917.3497 [Calcd for $C_{54}H_{54}O_{12}Na$ (M^++Na) 917.3510].

8b: Colorless foams; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.03 (6H, s, *gem*-Me), 1.08 (3H, d, J=6 Hz, 9-Me), 1.52 (2H, m, 8-H_2), 1.56 (3H, s, 5-Me), 1.61 (1H, t, J=12 Hz, 2ax-H), 1.81 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), *ca.* 1.88 (1H, m, 7-H), 2.13 (1H, br dd, J=16.5, 10 Hz, 4ax-H), *ca.* 2.25 (1H, m, 7-H), 2.36 (1H, br dd, J=16.5, 6 Hz, 4eq-H), 3.85 (1H, sext, J=6 Hz, 9-H), 4.15 (1H, ddd, J=10, 5.5, 3.5 Hz, 5′-H), 4.49 (1H, dd, J=12, 5.5 Hz, 6′-H), 4.65 (1H, dd, J=12, 3.5 Hz, 6′-H), 4.92 (1H, d, J=8 Hz, 1′-H), 5.21 (1H, m, 3-H), 5.50 (1H, dd, J=10, 8 Hz, 2′-H), 5.68 (1H, t, J=10 Hz, 4′-H), 5.91 (1H, t, J=10 Hz, 3′-H), 7.25—7.58 (15H, m, ArH), 7.82—8.06 (10H, m, ArH). SIMS *m*/*z*: 917.3511 [Calcd for $C_{54}H_{54}O_{12}Na$ (M^++Na) 917.3510].

13a: Colorless foams; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.92, 0.98 (each 3H, s, *gem*-Me), 1.33 (3H, d, J=6 Hz, 9-Me), 1.48 (3H, s, 5-Me), 1.49 (1H, t, J=12 Hz, 2ax-H), 1.56—1.77 (2H, m, 8-H_2), 1.80 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 1.87 (1H, br dd, J=16.5, 9.5 Hz, 4ax-H), 2.01 (2H, br t, J=8.5 Hz, 7-H_2), 2.13 (1H, br dd, J=16.5, 5 Hz, 4eq-H), 3.98 (1H, m, 3-H), 4.19 (1H, ddd, J=9.5, 6, 3.5 Hz, 5′-H), 4.51 (1H, dd, J=12, 6 Hz, 6′-H), 4.63 (1H, dd, J=12, 3.5 Hz, 6′-H), 4.98 (1H, d, J=8 Hz, 1′-H), 5.11 (1H, sext, J=6 Hz, 9-H), 5.50 (1H, dd, J=9.5, 8 Hz, 2′-H), 5.62 (1H, t, J=9.5 Hz, 4′-H), 5.91 (1H, t, J=9.5 Hz, 3′-H), 7.04—7.58 (15H, m, ArH), 7.82—8.06 (10H, m, ArH). SIMS *m*/*z*: 917.3521 [Calcd for $C_{54}H_{54}O_{12}Na$ (M^++Na) 917.3510].

13b: Colorless foams; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.94, 0.95 (each 3H, s, *gem*-Me), 1.33 (3H, d, J=6 Hz, 9-Me), 1.49 (3H, s, 5-Me), 1.49 (1H, t, J=12 Hz, 2ax-H), 1.66 (2H, m, 8-H_2), 1.81 (1H, ddd, J=12, 3.5, 2 Hz, 2eq-H), 1.87 (1H, br dd, J=16.5, 10 Hz, 4ax-H), *ca.* 1.90 (1H, m, 7-H), *ca.* 2.08 (1H, m, 7-H), 2.12 (1H, br dd, J=16.5, 5.5 Hz, 4eq-H), 3.98 (1H, m, 3-H), 4.19 (1H, ddd, J=9, 6, 3.5 Hz, 5′-H), 4.52 (1H, dd, J=12, 6 Hz, 6′-H), 4.63 (1H, dd, J=12, 3.5 Hz, 6′-H), 4.98 (1H, d, J=8 Hz, 1′-H), 5.11 (1H, sext, J=6 Hz, 3-H), 5.50 (1H, dd, J=9.5, 8 Hz, 2′-H), 5.62 (1H, t, J=9.5 Hz, 4′-H), 5.91 (1H, t, J=9.5 Hz, 3′-H), 7.24—7.58 (15H, m, ArH), 7.82—8.06 (10H, m, ArH). SIMS *m*/*z*: 917.3522 [Calcd for $C_{54}H_{54}O_{12}Na$ (M^++Na) 917.3510].

References

1) Straubinger M., Knapp H., Oka N., Watanabe N., Winterhalter P., *J. Agric. Food Chem.*, **45**, 4053—4056 (1997).
2) Sefton M. A., Skouroumounis G. K., Massy-Westropp R. A., Williams P. J., *Aust. J. Chem.*, **42**, 2071—2084 (1989).
3) Yamano Y., Watanabe Y., Watanabe N., Ito M., *Chem. Pharm. Bull.*, **48**, 2017—2018 (2000).
4) Yamano Y., Watanabe Y., Watanabe N., Ito M., *J. Chem. Soc.*, *Perkin Trans. 1*, **2002**, 2833—2844 (2002).
5) Matsumura K., Hashiguchi S., Ikariya T., Noyori R., *J. Am. Chem. Soc.*, **119**, 8738—8739 (1997).
6) Kunz H., Harreus A., *Liebigs Ann. Chem.*, **1982**, 41—48 (1982).
7) Otsuka H., *Phytochemistry*, **37**, 461—465 (1994).
8) Kasai R., Suzuo M., Asakawa J., Tanaka O., *Tetrahedron Lett.*, **1977**, 175—178 (1977).
9) Kasai R., Okihara M., Asakawa J., Mizutani K., Tanaka O., *Tetrahedron*, **35**, 1427—1432 (1979).